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Short communication

A microbial fluidized electrode electrolysis cell (MFEEC) for enhanced hydrogen production

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HIGHLIGHTS

- A microbial fluidized electrode electrolysis cell was designed for H_2 production.
- The total cumulative charge was increased 20% by using the MFEEC.
- Hydrogen yields were increased from 0.59 to 0.82 mol-H_2/mol-acetate using the MFEEC.

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ABSTRACT

A microbial fluidized electrode electrolysis cell (MFEEC) was used to enhance hydrogen gas production from dissolved organic matter. Flowable granular activated carbon (GAC) particles were used to provide additional surface area for growth of exoelectrogenic bacteria. The use of this exoelectrogenic biofilm on the GAC particles with fluidization produced higher current densities and hydrogen gas recoveries than controls (no recirculation or no GAC), due to intermittent contact of the capacitive particles with the anode. The total cumulative charge of 1688C m^{-2} with the MFEEC reactor (a recirculation flow rate of 19 mL min^{-1}) was 20% higher than that of the control reactor (no GAC). The highest hydrogen gas yield of 0.82 ± 0.01 mol-H_2/mol-acetate (17 mL min^{-1}) was 39% higher than that obtained without recirculation (0.59 ± 0.01 mol-H_2/mol-acetate), and 116% higher than that of the control (no GAC, without recirculation). These results show that flowable GAC particles provide a useful approach for enhancing hydrogen gas production in bioelectrochemical systems.

1. Introduction

The production of hydrogen from renewable resources has gained increasingly attention as it is a clean energy carrier with no carbon emission [1,2]. Bioelectrochemical systems, such as microbial electrolysis cells (MECs), can be used to produce hydrogen from biomass in wastewater with a much lower energy input than electrochemical systems based on water splitting reactions [3]. In an MEC, exoelectrogenic bacteria on the anode spontaneously donate electrons to the anode while oxidizing the organic matter in the wastewater, and a small voltage is applied to overcome the thermodynamic limit for effective hydrogen evolution [4,5].

Anode performance can limit performance in MEC reactors, where increased anode biomass is needed for better electrochemical and treatment performance [6]. The exoelectrogenic bacteria in an MEC are typically present only as a biofilm on the conductive surface of the anode. Therefore, the anode biomass depends directly on the total effective surface area per volume of the reactor and the thickness of the biofilm [7,8]. Diffusion limitations can occur when the biofilm becomes thick. Substrate needs to diffuse into the anode biofilm to provide the fuel for those exoelectrogenic bacteria closest to the anode, while the bacteria at the outer part of the biofilm need to effectively pass electrons to the anode. Recently, a fluidized bed technology was proposed to overcome some of the substrate diffusion limitations for the anode [9]. Introducing fluidized granular activated carbon (GAC) particles into the reactor provides an approach to enhance anode biomass [10], as the GAC particles have good electrical conductivity and a

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high specific surface area needed for biofilm attachment [11]. Previous results using packed bed continuous-flow MEC reactor with GAC particles show that the GAC can enhance columbic efficiency, hydrogen yield and reduce internal resistance due to the large specific surface area of GAC particles [12]. However, in a packed-bed reactor, the packing density of the GAC is limited by the reactor volume. More importantly, due to the irregular shape of GAC particles and the bed porosity, the electrical contact between GAC particles and the current collector is small, and thus there is a higher electrical resistance for the particles more distant from the current collector. This limits the useful amount of GAC particles that can be placed into a packed bed. In addition, the packed bed could clog with biomass. By fluidizing the GAC particles, they can all individually contact the current collector, and they will not clog. Our previous results also show that the GAC particles coated with exoelectrogenic biofilm exhibited capacitor-like behavior in a microbial fuel cell (MFC). By using flowable GAC particles in an MFC, the reactor had enhanced current and power production due to the discharge of the electroactive biofilm (on GAC particles) when they made intermittent contact with the current collector [13]. This suspended biomass made full use of the reactor volume, and enhanced COD removal and coulombic efficiencies. The flowable GAC particles in the MFC were shown to contribute significantly to improved power density compared to a packed-bed MFC reactor, due to the fact that fluidized bed operation enabled more efficient electrical discharge from GAC particles.

In this study, we developed a different reactor configuration, called a microbial fluidized electrode electrolysis cell (MFEEC), to examine the use of fluidized GAC particles for enhanced H_2 gas production in an MEC-based reactor, rather than electrical power production in an MFC. This new MFEEC configuration was designed to make more optimal use of the bio-capacitive exoelectrogenic biofilm in a fluidized reactor. We compared the hydrogen production with and without the presence of GAC particles, and also investigated the effect of recirculation flow rates on the hydrogen yield in the MFEEC reactors.

2. Materials and methods

2.1. Reactor construction

The MFEEC reactor was constructed with a clear polyvinyl chloride (PVC) tube (height $h = 28$ cm, diameter $d = 1.3$ cm, empty bed volume of 40 mL) (Fig. 1). GAC particles (1.0 g, 40 × 40 mesh, DARCO MRX M-1721, Norit Americas Inc.) were filled into the MFEEC reactor as the flowable anode for biofilm growth. Nylon mesh (60 × 60) was placed at the bottom of the reactor to prevent GAC particles from leaking outside of the tube during flow recirculation. The anode current collector was a graphite block (7 cm × 0.5 cm × 0.3 cm, GM-10) placed at the bottom of the MFEEC reactor. In order to remove the impurities on the anode surface, the graphite block was cleaned by submerging it in 1 M HCl overnight, followed by rinsing using ultrapure water (18.2 MΩ cm at 25 °C, Milli-Q water system, EMD Millipore Corporation, USA) [14]. The distance between the bottom of the graphite block and the GAC particles layer was ~2 cm. In order to avoid the short circuiting between the conductive fluidized GAC particles and the cathode, a cylindrical stainless steel mesh cathode ($d = 1.0$ cm, $h = 10$ cm, type 304, 60 × 60 mesh, McMaster-Carr) was placed on the top of the reactor (Fig. 1). An Ag/AgCl reference electrode (RE-5B, +209 mV vs. a standard hydrogen electrode, SHE; Bioanalytical Systems, Inc.) was inserted between the two electrodes. The control reactor had the same configuration as the test reactor, but it lacked GAC particles. All other operational conditions were the same for the MFEEC and control reactors.

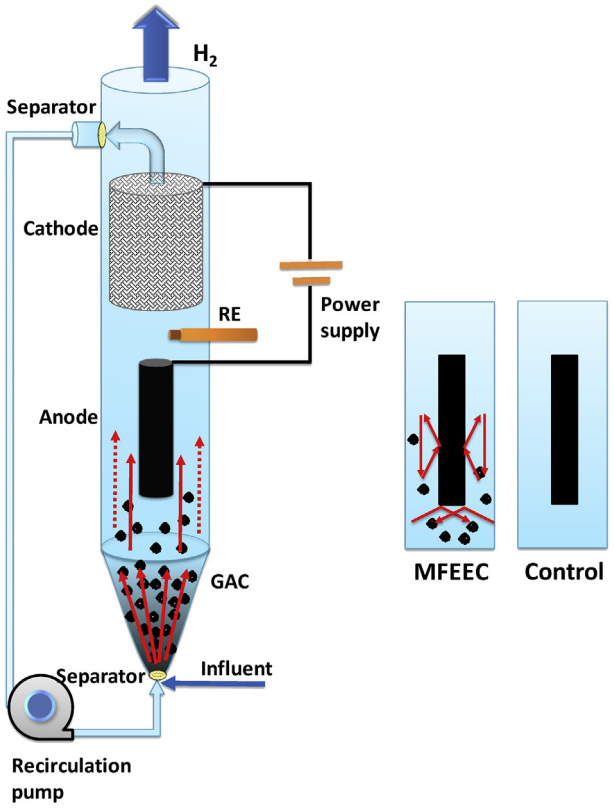

Fig. 1. Schematic diagram of microbial fluidized electrode electrolysis cell.

2.2. Reactor operation

In order to minimize the possibility for methane production, the reactors were inoculated with *Geobacter sulfurreducens* PCA (ATCC 51573). Although sterile conditions were not maintained, methane was not detected in the product gas. The medium for reactor operation contained 0.82 g L^{-1} sodium acetate, 1.5 g L^{-1} of NH_4Cl, 0.6 g L^{-1} of NaH_2PO_4, 0.1 g L^{-1} of KCl, 2.5 g L^{-1} of $NaHCO_3$, 10 mL of minerals, and 10 mL of vitamins [15]. The medium was sparged with anaerobic gas (N_2:CO_2, 80%:20%) to adjust the pH to ~7.0, and autoclaved at 121 °C. A voltage of 0.8 V was applied to the circuit using a power supply (model 3645A; Circuit Specialists, Inc.) for hydrogen evolution (except as noted), with an external resistor of 10 Ω in the circuit to allow measurement of current based on the voltage across the resistor [3]. In some tests, a set anode potential of −0.2 V (vs. SHE) was used to investigate the charge and discharge processes with fluidized GAC particles [13]. All reactors were operated in fed-batch mode in a temperature controlled room (30 °C), with substrate replacement when the current decreased to <0.03 mA.

GAC particles were fluidized by liquid recirculation using a peristaltic pump (model 7523-90, Masterflex, Vernon Hills, IL). The minimum recirculation flow rate needed to fluidize the GAC particles was 15 mL min^{-1}. The maximum flow rate was 19 mL min^{-1}, as higher flow rates produced shorting circuiting between the particles and the cathode (i.e. discharge of current from the GAC biofilms to the cathode, without current generation). Therefore, recirculation the flow rates were varied from 0 to 15, 17, or 19 mL min^{-1}.

2.3. Measurements and analyses

Current (I) was measured across an external resistor (10 Ω) and recorded at 10 min intervals using a multimeter (Keithley

Instrument, OH) connected to a personal computer. The gas was collected in a gas bag (0.1 L, Cali-5-Bond, Calibrated Instruments Inc.), and the total gas volume was measured using a glass syringe. Gas chromatography (SRI Instruments, Torrance, CA) was used to determine H_2, N_2, CO_2, and CH_4 concentrations in the reactor headspace as well as in the gas bags as previously described [3]. The total cumulative charge (Q), coulombic efficiency (CE), and overall hydrogen recovery ($r_{H_2,\,COD}$) were calculated as previously described [4,16]. The pumping power requirement for flow recirculation, P_{pump} (kW), was calculated as: $P = Q\gamma E/1000$, where Q is flow rate ($m^3\ s^{-1}$), γ is the specific gravity of water (9800 N m^{-3}), and E is the hydraulic pressure head (m) [17]. The daily energy requirement for pumping was then calculated as W (kJ d^{-1}) = 86,400P.

3. Results and discussion

3.1. Current generation and charge/discharge experiments

After consistent and repeatable cycles of current generation, the reactors were operated for an additional month to ensure stable conditions prior to tests. The charge/discharge behavior was examined at a set anode potential of −0.2 V, with periodic circuit interruption under different flow rates. The use of the flowable GAC anode in the MFEEC significantly improved current production (Fig. 2A). At a flow rate of 15 mL min^{-1}, the GAC particles intermittently struck the graphite anode and discharged electrons to the graphite block. The current density was stable at 1.37 A m^{-2}, which was 14% higher than that of the control reactor (without recirculation, 1.20 A m^{-2}) or 25% higher than that obtained without GAC and recirculation conditions (1.10 A m^{-2}). This increase in current density with GAC fluidization was therefore mainly due to extra electrons discharged from the exoelectrogenic biofilm on the GAC particles.

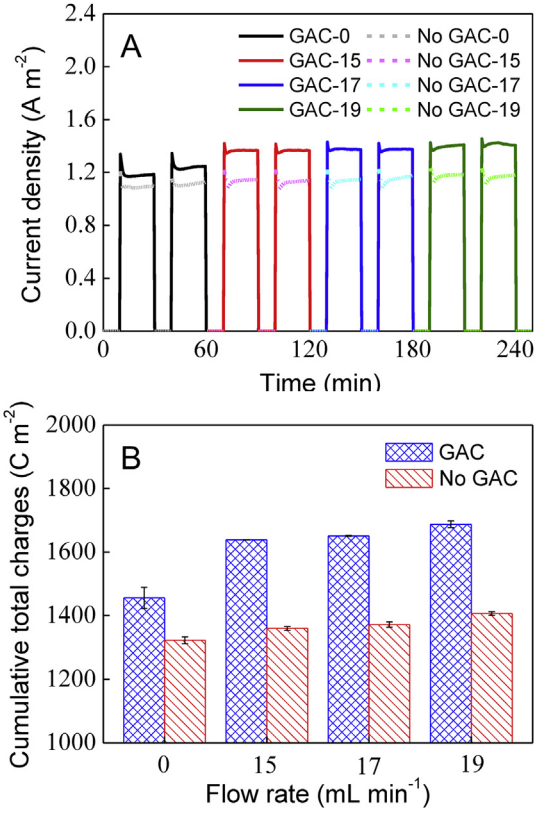

Fig. 2. (A) The current densities of MFEEC and control reactor with 10 min of charging (open circuit) and 20 min discharging (poised anode potential at −0.2 V vs. SHE). (B) Amount of cumulative total charges of MFEEC and control reactor. (GAC, MFEEC reactor with GAC particles; No GAC, control reactor without GAC particles).

Current density was further increased to 1.42 A m^{-2} by using a higher flow rate of 19 mL min^{-1} due to more frequent collisions of GAC with the anode. In the control reactor without GAC particles, there was only a slight increase from 1.10 A m^{-2} to 1.16 A m^{-2} when the flow rate was increased from 0 to 19 mL min^{-1}, demonstrating only a small influence on the current production by water motion. At low current densities, overpotentials primarily resulted from activation and ohmic losses, but not mass transfer limitations, and therefore greater turbulence produced by the increase in flow rate did not lead to appreciable improvements in performance with the control reactor. These results were consistent with previous findings that GAC particles can discharge electrons and increase current production by intermittent contact with a current collector [13].

As a result of increased current production, the total cumulative charge of MFEEC reactor with GAC particles was higher than that without GAC particles in the control reactor (Fig. 2B). When fluidizing GAC particles were coated with exoelectrogenic biofilms, the total cumulative charge significantly increased from 1456C m^{-2} (no recirculation) to 1638C m^{-2} at flow rate of 15 mL min^{-1}. This 13% increase in charge was much greater than that obtained with recirculation but no GAC particles (3%) in the reactor (control). This indicated that the increase in total cumulative charge of MFEEC was due to the capacitive GAC particles and not mass transfer due to the fluid recirculation. When the flow rate was further increased from 15 mL min^{-1} to 19 mL min^{-1}, the total cumulative charge was 1688C m^{-2}, which was 20% higher than that of the control reactor (no GAC).

3.2. Hydrogen gas production, coulombic efficiency, COD removal and overall hydrogen recovery

The MFEEC reactor with GAC particles had a significant increase in the hydrogen production rate and sustained a high hydrogen level under different flow rate conditions compared to the control reactor (Fig. 3A). The MFEEC reactor with the flow rate of 17 mL min^{-1} produced a highest hydrogen gas yield of 0.82 ± 0.01 mol-H_2/mol-acetate, which was 39% greater than that obtained without recirculation (0.59 ± 0.01 mol-H_2/mol-acetate), and 116% higher than the control reactor that did not contain GAC particles (0.38 ± 0.02 mol-H_2/mol-acetate). Recirculation of the fluid in the control reactor (no GAC) reduced hydrogen gas yield from 0.38 ± 0.02 mol-H_2/mol-acetate (no recirculation) to 0.27 ± 0.01 mol-H_2/mol-acetate (19 mL min^{-1}). This reduction in H_2 gas recovery was likely due to enhanced hydrogen recycling with flow recirculation.

The COD removals using the MFEEC with GAC particles did not change appreciably by varying the flow rate (0–19 mL min^{-1}). The average COD removal ranged from 59% to 64%, which was similar to those obtained using the control reactor (56%–65%) (Fig. 3B). CEs were much larger than 100% with flow recirculation for both MFEEC and control reactors. The highest CE for the MFEEC was 188% at flow rate of 17 mL min^{-1}, with 178% at 19 mL min^{-1}, and 166% at 15 mL min^{-1} (166%) (Fig. 3B). The CEs of the control reactors (no GAC) were similarly enhanced by flow rate, with CEs ranging from 149% (17 mL min^{-1}) to 125% (19 mL min^{-1}). Without recirculation, CEs decreased to <100% (90%, with GAC, 89% without GAC). CEs >100% were due to H_2 gas recycling, where H_2 produced by the cathode is used by anode

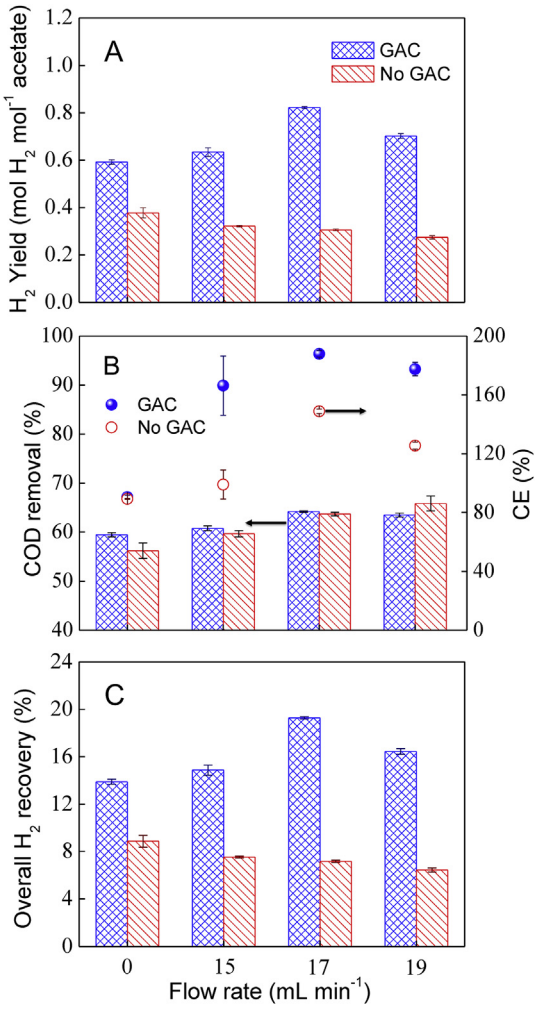

Fig. 3. (A) H_2 yield, (B) COD removal and coulombic efficiency, (C) overall hydrogen recovery for MFEEC and control reactor (GAC, MFEEC reactor with GAC particles; No GAC, control reactor without GAC particles).

bacteria [18,19]. The results demonstrate that flow recirculation enhanced H_2 gas utilization by the anode, which produced CEs larger than 100% and reduced net hydrogen yields. Future reactor designs will be needed that have a separator that avoids recirculation of the anolyte past the cathode.

The overall hydrogen recovery of MFEEC was significantly higher using the GAC particles than the control reactor without GAC particles, demonstrating that addition of the GAC particles in the reactor improved the MEC performance (Fig. 3C). When the MFEEC was recirculated, the MFEEC reactor produced a maximum overall hydrogen recovery of 19.3% at a flow rate of 17 mL min^{-1}, which was 39% higher than that without recirculation (13.9%). This increase in overall hydrogen recovery indicated that recirculation is needed to enhance the overall hydrogen recovery with the GAC particles. Different from the MFEEC reactor, the overall hydrogen recovery of the control reactor slightly decreased with flow recirculation, likely due to both relatively less current output and the hydrogen gas recycling on the anode.

3.3. Energy analysis

The pumping energy for flow recirculation was estimated to be 0.67×10^{-3} kJ d^{-1}. Under the flow rate of 17 mL min^{-1}, hydrogen gas production increased by 0.4×10^{-4} mol d^{-1}. Assuming an energy yield based on hydrogen gas combustion of 286 kJ mol^{-1} [20], the enhanced hydrogen production increased the energy yield to 1.14×10^{-2} kJ d^{-1}, which is ~17 times of the required pumping energy for the MFEEC system. Thus, the energy needed for pumping in the MFEEC was only <6% of the energy yield of the produced hydrogen.

4. Conclusions

A new type of fluidized bioelectrochemical reactor system was examined to enhance hydrogen production from biomass in wastewater. Fluidized GAC particles, used in the reactor to provide extra surface area for exoelectrogenic biofilm growth, functioned as an additional flowable anode. The MFEEC with fluidized GAC particles increased current by 20% and hydrogen yields by 116%, compared to those of the control reactor (no GAC), due to the intermittent discharge of the GAC particles on the fixed anode. These results indicate that the MFEEC could be effectively used to enhance hydrogen gas production from dissolved organic matter, such as that in a wastewater.

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